

Ethylphyllotaonin.

		Calculated.			
		$C_{20}H_{19}N_3O_2(OC_2H_5)$. $C_{40}H_{38}N_6O_5(OC_2H_5)$. $C_{41}H_{41}N_6O_5(OC_2H_5)$.			
	Found.				
C	69·22	69·84	69·32	69·54	
H	6·04	6·35	5·91	6·19	
N	11·40	11·11	11·55	11·32	

Acetylphyllotaonin.

		Calculated.			
		$C_{20}H_{19}N_3O_2(OAc)$. $C_{40}H_{38}N_6O_5(OAc)$. $C_{41}H_{41}N_6O_5(OAc)$.			
	Found.				
C	67·95	67·34	68·01	68·25	
H	6·17	5·61	5·53	5·82	

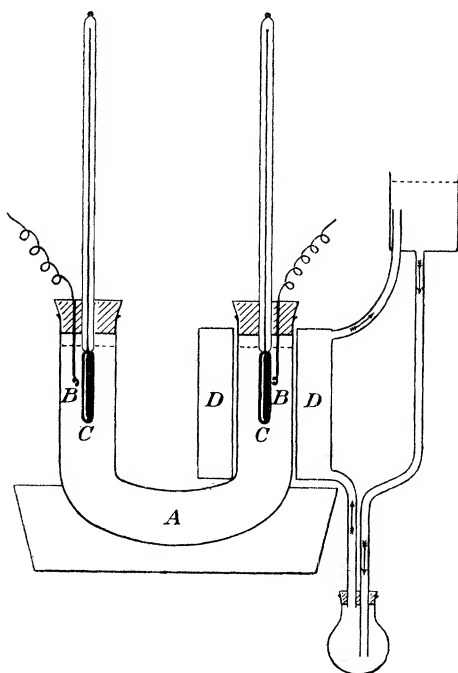
VI. "Thermo-electric Properties of Salt Solutions." By GEORGE FREDERICK EMERY, B.A., LL.M., of the Inner Temple, late Scholar of Trinity College, Cambridge. Communicated by Professor J. J. THOMSON, F.R.S. Received February 8, 1894.

The thermo-electrical properties of solutions have not hitherto received much attention from physicists. If we form a circuit of two substances, one a metallic wire and the other a solution, and arrange it so that the junctions between the metal and the liquid are at different temperatures, we generally find that an electromotive force is developed in the circuit which varies in magnitude nearly in proportion to the difference of temperature between the junctions, and which, in comparison with the ordinary thermo-electromotive forces in metallic circuits, is very considerable. Up to the present time, as far as I am aware, the only extensive measurements of such thermo-electric forces are those of M. Bouty ('Journ. de Phys.,' vol. 9). He concludes that for a given difference of temperature between the junctions when the metal is constant the E.M.F. is nearly independent of the nature and strength of the solution (the solution being of some salt of the metal used).

The object of my experiments has been to see how far this is true, and to find out how (in the event of its not being strictly true) the E.M.F. varies with variations both in the strength and in the nature of the solution. The results show that both have considerable influence on the magnitude of the E.M.F.

My method of observation is as follows: the solution to be examined is put in a U-tube (fig. 1, A), in each limb of which is one of the ends of metal, which we may for convenience call electrodes, BB.

FIG. 1.



Close to each electrode is the bulb of a thermometer, C, graduated to one-fifths of a degree Centigrade. One limb of the U-tube is surrounded by a water-jacket, DD, which is heated by an ordinary circulating arrangement, so that its temperature can be regulated as desired. (See fig. 1.) The E.M.F. between the electrodes is balanced against a branch of a circuit of about 20,000 ohms through which a pair of Leclanché cells are kept closed, and the value of an ohm in E.M.F. is measured against a Clarke cell.

At the commencement of each experiment, when both electrodes were at the same temperature, there was very often a slight E.M.F. between them. This was carefully read, and then the water-jacket was gradually heated and the readings of the thermometers were taken as the E.M.F. passed through, values represented by definite numbers of ohms generally differing by 5 or 10. The readings at the highest temperature were very carefully taken, and then the whole was allowed to cool, more readings being taken as the temperature fell. The value of any particular experiment is roughly given by the closeness of the readings for corresponding differences of temperature, while the temperature was rising and falling. In some series of observations the temperature was allowed to vary very slowly, so as

to give accurate readings all through and enable me to get a curve showing the connection between E.M.F. and difference of temperature. In every case this was very nearly a straight line, and most of the experiments were made pretty quickly so as to get accurate readings for the highest and lowest temperatures, while those for intermediate points served to show if any irregularity had taken place from secondary causes, and form a check on the accuracy of the whole. If the readings are not steady or differ much for corresponding points on rising and falling temperatures, I do not, as a rule, attach any value to that experiment. A change of $\frac{1}{16}^{\circ}$ C. in the temperature of one of the junctions gave an easily noticeable deflection to the galvanometer spot.

For convenience I have used the symbol $\mathcal{J}$ for the electromotive force per 1° C., and the unit in terms of which $\mathcal{J}$ is given is 10^{-4} volts per 1° C.

The value of $d\mathcal{J}/dt$ is in all cases very small compared with that of $\mathcal{J}$, and appears to vary in sign for different solutions.

Assuming, then, that $d\mathcal{J}/dt = 0$, as is approximately the case, my object was to find the variation of $\mathcal{J}$ with the strength of the solution.

I made a long series of experiments with six salts, acetate, chloride, and sulphate of zinc, and sulphate, nitrate, and acetate of copper. Nitrate of zinc and chloride of copper gave no results as they appeared to attack the electrodes. In a whole series of experiments on one salt I used the same lot of boiled distilled water and the same stock solution, which was diluted down to the required strength. I think, therefore, that any small effect due to impurities in the water may be safely taken to be a constant. The salts were all as pure as I could obtain, and the stock solution was kept for a long time over oxide or carbonate so as to neutralise any free acid as far as was possible.

I found considerable variations in the value of $\mathcal{J}$ when the concentration of the solution was varied, and to show these I have plotted curves (fig. 2), whose ordinates are equal to $\mathcal{J}$, and abscissæ are the corresponding concentrations in gram molecules per litre of volume. For very small concentrations it seems impossible to observe $\mathcal{J}$ accurately, and the parts of the curves corresponding to very small concentrations I have extra-polated as well as I can. For zero concentration the curves all appear to start from somewhere about $\mathcal{J} = 8.6$ at an angle to the axes, and then as concentration increases the curves bend round more or less sharply till they are nearly parallel to the axis of concentration. It will also be observed that for some salts $\mathcal{J}$ increases with increasing concentration, while for others it decreases, so that for thermo-electrical purposes we may divide salts into positive and negative according as the value of $\mathcal{J}$ for the solution is greater or less than its apparent value for pure water. In all the aqueous solutions

which I examined the current would go from hot to cold through the solution.

With the zinc salts I always used amalgamated zinc electrodes coated with sealing-wax or india-rubber where they entered the solution. I always found these very satisfactory; there was usually no E.M.F. between them when at the same temperature. Unamalgamated zinc is absolutely useless, as the E.M.F. flies about in a perfectly wild way. The following are the values found for $\mathcal{J}$:—

Chloride of Zinc in Water, A, fig. 2.

Concentration	= 0.4888	$\mathcal{J}$ = 6.609
„	= 0.2444	$\mathcal{J}$ = 6.868
„	= 0.1222	$\mathcal{J}$ = 7.295
„	= 0.0611	$\mathcal{J}$ = 7.89
„	= 0.0244	$\mathcal{J}$ = 8.14
„	= 0.0122	$\mathcal{J}$ = 8.3—8.4
Unknown	„ strong	$\mathcal{J}$ = 6.515

All the experiments on this salt were very satisfactory in every way.

Acetate of Zinc in Water, B.

Concentration	= 0.872	$\mathcal{J}$ = 6.852
„	= 0.436	$\mathcal{J}$ = 6.854
„	= 0.1744	$\mathcal{J}$ = 7.17
„	= 0.0872	$\mathcal{J}$ = 7.38
„	= 0.0436	$\mathcal{J}$ = 7.55
„	= 0.022	$\mathcal{J}$ = 7.9—8.1

This salt gave very satisfactory results.

Sulphate of Zinc in Water, C.

Concentration	= 0.525	$\mathcal{J}$ = 8.95
„	= 0.261	$\mathcal{J}$ = 8.8
„	= 0.0645	$\mathcal{J}$ = 8.636
„	= 0.0161	$\mathcal{J}$ = 8.55

This salt was not so satisfactory as those above, but the results are sufficient to show that the sulphate is thermo-electrically positive in aqueous solution.

With the copper salts I came to the conclusion, after trying several forms of electrode, that the most satisfactory consisted of a short length of fine wire projecting from the end of a glass tube, which was drawn out and stopped with shellac. The following results were obtained:—

Sulphate of Copper, D.

Concentration	= 0.6032	$\mathcal{J}$ = 7.8
„	= 0.2011	$\mathcal{J}$ = 8.05
„	= 0.1005	$\mathcal{J}$ = 8.3
„	= 0.0402	$\mathcal{J}$ = 8.5

These were all very satisfactory. The value of $\mathcal{J}$ for the strongest solution agrees with that found by M. Bouty.

Nitrate of Copper, E.

Concentration	= 0.384	$\mathcal{J}$ = 6.5
„	= 0.192	$\mathcal{J}$ = 6.6—7
„	= 0.096	$\mathcal{J}$ = 7.15—7.31
„	= 0.0384	$\mathcal{J}$ = 7.8
„	= 0.0137	$\mathcal{J}$ = 8.5

Another stock solution gave—

Concentration	= 0.25	$\mathcal{J}$ = 6.618
„	= 0.5	$\mathcal{J}$ = 5.583—5.577
„	= 1.0	$\mathcal{J}$ = 6, also 7.176—7.083
„	= 2.0	$\mathcal{J}$ = 7.018
„	= 4.0	$\mathcal{J}$ = 6.39

These last very strong solutions do not seem to follow any rule, the last two were quite oily. The 0.25 concentration is the only one within the range of the first set of experiments with which it fits in very fairly.

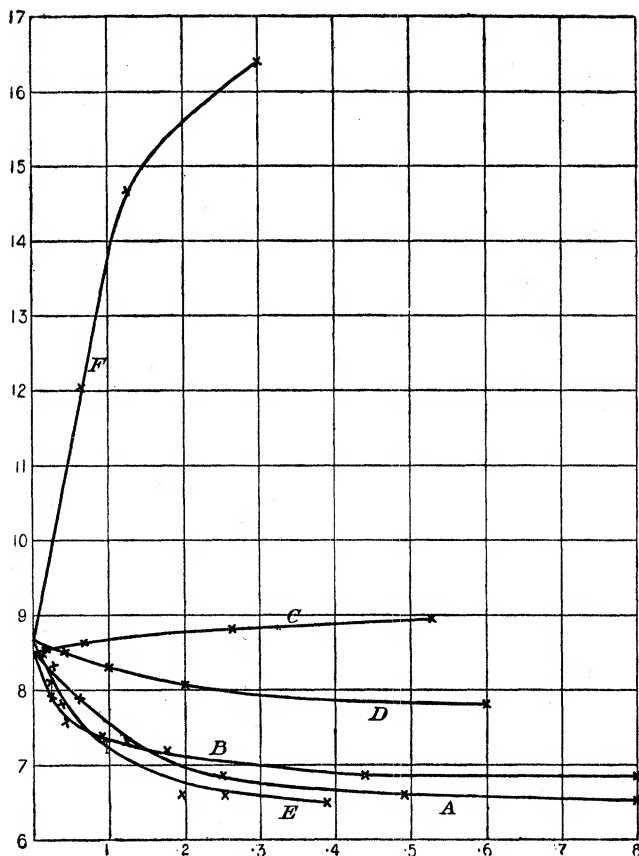
Acetate of Copper, F.

Concentration	= 0.25	$\mathcal{J}$ = 16.4	It may be higher, but < 17.5
„	= 0.125	$\mathcal{J}$ = 14.7	Varied from 13.7—15.6
„	= 0.0625	$\mathcal{J}$ = 12.1	

This last of the copper salts was not at all satisfactory, but the results with it are very interesting, as the values of $\mathcal{J}$ are all far above anything others measured. As the temperature rose the E.M.F. generally varied in an irregular way, rising at times more quickly than would be right, but as the temperature fell the E.M.F. usually fell pretty steadily, and the values deduced from the fall are those given; they were all repeated, and the value given is what appears best. The value 12.1 for the last concentration was very steady.

After these experiments the solution stood in a stoppered bottle, and some bright blue crystals separated out of the liquid.

FIG. 2.



The results were somewhat changed by this, and the following were obtained, which though rather irregular show the great thermo-electric effect in this solution.

Acetate of Copper.

Concentration = 0.125	$\theta = 15$
„ = 0.0625	$\theta = 13-16$
„ = 0.05	$\theta = 15.6-17.2$
„ = 0.025	$\theta = 17.3$
„ = 0.01	$\theta = 17.1$
„ = 0.005	$\theta = 13.5-15$
„ = 0.0025	$\theta = 13.7$
„ = 0.001	$\theta = 10.1$

The weakest of these solutions gave the best results, it seemed as if the stronger the solution was the more irregular the E.M.F. became. All that can be said is that acetate of copper is very strongly thermoelectrically positive, and that a very minute quantity in water has a very great effect on the value of $\mathcal{J}$.

These experiments appear to show that a great part of the quantity $\mathcal{J}$ is due to the water, and that the presence of a salt in solution may increase or diminish the value of $\mathcal{J}$ according to the nature of the salt. The next step was to see how far this effect was an additive one, and for this various mixtures of the above salts were used. The value for water appears to be in the neighbourhood of $\mathcal{J} = 8.6$, but it cannot be measured directly, as with pure water the results are very irregular. The following table gives the value of $\mathcal{J}$ as observed for the mixture, the values for the separate salts of the same strength, and the value which $\mathcal{J}$ would have if water were 8.6 and the differences for the salts were additive.

$\mathcal{J}$ observed.		$\mathcal{J}$ single salts.	$\mathcal{J}$ calculated.
6.3	} = {	ZnCl ₂ 0.2444	} 5.122
6.05		ZnAc ₂ 0.436	
6.473	} = {	ZnCl ₂ 0.1222	} 5.665
6.373		ZnAc ₂ 0.218	
6.28	} = {	Cu(N ₂ O ₃) ₂ 0.271	} 6.2
		CuSO ₄ 0.2011	
6	} = {	Cu(N ₂ O ₃) ₂ 0.137	} 6.9
		CuSO ₄ 0.1005	
8.94	} = {	Cu(N ₂ O ₃) ₂ 0.125	} 8.35—9.65
		CuAc ₂ 0.025	
7.9	} = {	CuAc ₂ 0.05	} 7.9
		CuSO ₄ 0.3	

With brass—

6.4	} = {	ZnSO ₄ 0.174
		CuSO ₄ 0.4022

These results show that though the difference from the water value of $\mathcal{J}$ is not quantitatively additive, yet as far as direction is concerned the differences do add, with the exception of the mixture of copper sulphate and acetate, which turned quite milky during the heating, though there was no trace of irregularity in the change of E.M.F. In a case where the components are both negative $\mathcal{J}$ for the mixture is below either of the $\mathcal{J}$'s for the components, while for a mixture of a positive salt with a negative one the value of $\mathcal{J}$ is between those for the components. It will be noticed that in all the mixtures the salts have one common component, so that there cannot be any action between the two salts. These results for mixtures of salts seem to be of value as supporting the theory that the final $\mathcal{J}$ in a solution

is due to the superposing of a salt effect on that due to the water itself.

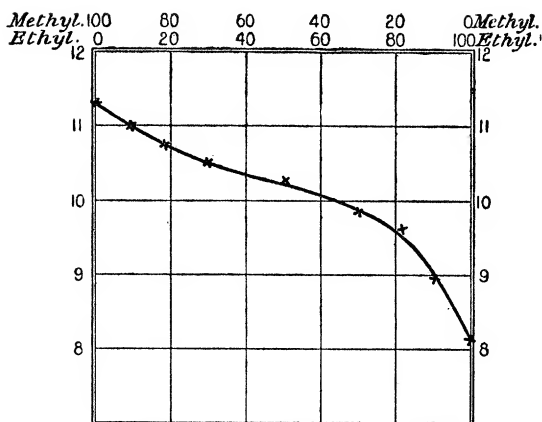
We see from these observations that for any given salt the value of $\mathcal{Q}$, starting from some value independent of the nature of the salt, tends to come to some value depending on the salt, and which does not vary much for solutions of moderate strength. The latter result was that obtained by M. Bouty; the former is believed to be new. In one of his series of experiments M. Bouty used very strong solutions of zinc chloride, and he found that as the strength of these was increased the value of $\mathcal{Q}$ rapidly diminished. This taken with the above results seems to show that, if we could trace the entire curve for this salt, taking the value of $\mathcal{Q}$ for all concentrations down to pure zinc chloride at one end and pure water at the other, we should have a curve with a point of inflexion somewhere about its middle. It would, of course, be well-nigh impossible to trace such a curve for any salt, but we can do something very nearly identical without any great difficulty. If we take two solvents, and while keeping the salt a fixed quantity use different mixtures of the solvents, we can get a complete curve for $\mathcal{Q}$, as it varies with the change of solvent. I made a large number of experiments on 1 per cent. solutions, or rather 1 gram per 100 c.c. solutions of cadmium bromide; these gave very good results with all the mixtures used. The electrodes were the exposed ends of sticks of cadmium, the sides being coated with glass. In each set I started with the solutions in pure solvents, and then mixed them so as to get the required mixture for each experiment.

With solutions of 1 gram per 100 c.c. in methyl alcohol and ethyl alcohol with their mixtures the following results were obtained :—

Methyl alcohol.	Ethyl alcohol.	$\mathcal{Q}$ (see fig. 3).
100·0	0	11·3
90·0	10·0	11·0
81·3	18·7	10·76
70·0	30·0	10·4—10·5
50·0	50·0	10·27
30·0	70·0	9·86
18·7	81·3	9·64
10·0	90·0	8·9
0	100·0	8·15

This gives us a curve with a point of inflexion similar to that suggested above as the probable shape of the complete curve for water and zinc chloride.

FIG. 3.



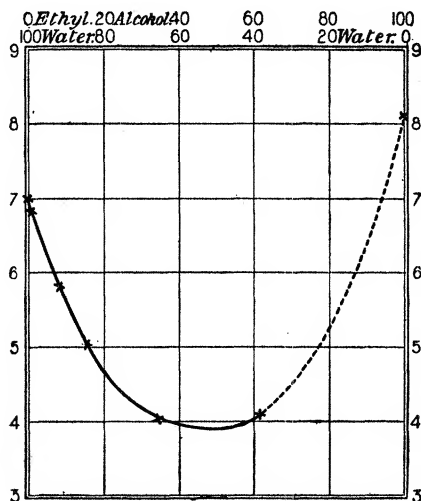
Solutions of 1 gram of cadmium bromide per 100 c.c. in ethyl alcohol and water gave the following results:—

Ethyl alcohol.	Water.	Sp. gr.	ρ (fig. 4).
0	100.0	1.00992	7.0
1.1	98.9	1.00384	6.86
10.0	90.0	0.99464	5.83
25.0	75.0	0.97825	5.053
50.0	50.0	0.93992	4.075
75.0	25.0	0.88472	4.123
100.0	0	0.81106	8.15

These results show a marked difference from those for mixtures of the two alcohols, methyl and ethyl. In the latter case we have an inflected curve, which is never far from the mean line which it would occupy, if ρ for the mixture were proportionally placed between the ρ 's for the pure liquids. In the present case, however, a very small admixture of either with the other causes a large drop in the value of ρ , and the curve lies almost entirely below its lower extremity. In both cases the ends are as symmetrical as the positions of the extremities will permit.

Now, the two pairs of solvents would appear to be good representatives of two classes of pairs of liquids. The two alcohols mix in a quiet way with no appearance of chemical action, or, if any, very little in the way of heat evolution and alteration of bulk, so that we might very well expect to find any property of the mixture not very different from the corresponding properties of the two components, and lying somewhere between them in value. In the case of a mixture of alcohol with water we have, on the contrary, large evolution of heat

FIG. 4.



and considerable alteration in bulk, so that we might expect to find a change in any physical property disproportionate to that usual in a case of simple mixture.

The variations in the value of J for these two pairs are very like those in the conductivity of different pairs of metals, for here again we have in some cases the conductivity of the mixture nearly equal to the mean conductivity of the components, while for other pairs the conductivity of a mixture is far lower than that of either component.

Besides the above sets of experiments, observations on a constant strength of a stock solution of zinc sulphate mixed down to a constant bulk per 5 c.c. of stock with various substances, gave the following results.

Water only	$J = 8.15$
10 per cent. alcohol.....	$J = 7.628$
20 " "	$J = 7.22$
30 " "	$J = 6.883$
40 " "	$J = 6.66$
10 grams sugar per 100 c.c.	$J = 8.127$
45 " "	$J = 8.04$
10 c.c. of a sodic sulphate solution per 100 c.c.	$J = 7.764$
20 " " " "	$J = 7.7$
30 " " " "	$J = 7.67$
20 " " " " + 10 c.c.	$J = 7.436$

All these were very satisfactory measurements. The zinc sulphate solution was not the same as that used before, and the value of $\mathcal{J}$ for the aqueous solution is considerably lower than any of those previously obtained. The great alteration in the value of $\mathcal{J}$ sometimes caused by comparatively slight changes in the quality of the solution makes it rather difficult to get the same results with two solutions which are apparently alike, and I do not think that this last value 8.15 need cause doubt as to the substantial accuracy of the previous results, since two at least of the previous set giving higher values for $\mathcal{J}$ appeared to be free from any objection.

It will be noticed that all the additions to this zinc sulphate solution caused a decrease in the value of $\mathcal{J}$, that for sugar, as might be expected from such an inactive substance, being least and nearly proportional to its amount. The presence of the sodic sulphate has considerable effect on the value of the change caused by 10 per cent. alcohol, reducing the decrease in $\mathcal{J}$ by about half its amount. The strength of the sodic sulphate added was too great to make the results very interesting, but I have no doubt that the curve would have come round to the zero at 8.15, like all the others.

Various strengths of cadmium bromide in alcohol, which was afterwards found not to be pure, were tried. The salt appeared to be pretty strongly positive, the values observed for $\mathcal{J}$ being—

For 0.4 per cent. solution $\mathcal{J} = 5.87$

1.0 " " $\mathcal{J} = 7$

4.0 " " $\mathcal{J} = 8.115$

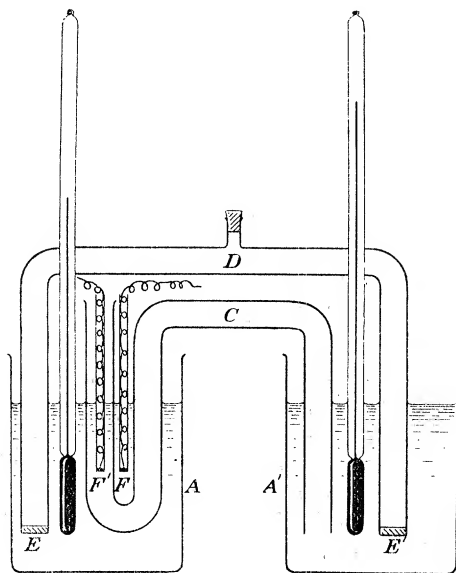
1 gram cadmium bromide in 100 c.c. of normal propyl alcohol gave $\mathcal{J} = 7.43$.

A few experiments of what are believed to be an entirely novel kind were made on the thermoelectric force generated in a purely liquid circuit, that is, in a circuit composed of two kinds of liquid, the junctions being at different temperatures. To measure this E.M.F. one of the liquids was divided, and between the extremities, which were kept at exactly the same temperature, two similar electrodes were inserted. For this the following apparatus (fig. 5) was used.

The method of observation was as follows:—

The beakers A, A' contain No. 1 liquid, as does the tube C. Of two tubes D, of which the ends are closed by porous plates, D 1 contains No. 1 liquid, and D 2 contains No. 2 liquid. The tube D 1 was placed in position, and when the temperature was steady the E.M.F. between F, F', which were at the same temperature connected by one fluid was measured. Then the tube D 1 was removed, tube D 2 inserted, and the E.M.F. taken as soon as the temperature was steady.

FIG. 5.



AA' are two beakers containing one of the liquids under examination, which we will call No. 1.

BB' are two thermometers for telling the temperature of the liquid in the beakers.

C is a bent tube full of No. 1 liquid, which is continuous between the end of C, which is under the liquid in A', and in which the electrode F' dips.

D is a syphon tube connecting the liquids in AA'; it is full of liquid No. 2, and is closed at its ends by porous plugs, EE', made of porous earthenware and fixed with shellac.

FF' are the electrodes, F being in beaker A, and F' in tube C, close to F, the bent part of C being in the beaker A.

The following results were obtained :—

With zinc sulphate 4 per cent. No. 1, zinc chloride weak as No. 2.

$E/(t' - t) = 1.36 \times 10^{-4}$ V for two observations with temperature differences 36.4 and 29.4.

With zinc acetate as No. 2—

$$t' - t = 15.6 \quad E/(t' - t) = 0.8 \times 10^{-4} \text{ V}$$

$$t' - t = 28.0 \quad E/(t' - t) = 1.05 \times 10^{-4} \text{ V}$$

$$t' - t = 30.3 \quad E/(t' - t) = 1.13$$

The latter are not so good as the first on zinc chloride, which gives about what we might expect from the difference of the $\mathcal{P}$'s of the two

salts. A few trials with alcohol in the D-tube were made, but were not very successful, owing to the rapid effects of diffusion in the A beaker constantly altering the E.M.F. at constant temperature.

Lastly, I endeavoured to prove by experiment that these thermo-electric forces at the junctions of metals and solutions are part of a system of reversible thermodynamic phenomena. For this to be true we require to prove the equation

$$\mathcal{Q} = dE/dt = H/t,$$

where H is the heat developed by the passage of unit of electricity across the junction, t is the absolute temperature of the junction, and $\mathcal{Q}$ is the quantity discussed above.

As far as I am aware, M. Bouty alone has attempted this previously ('Journ. de Phys.,' vol. 9). He used the plated bulbs of two similar thermometers as electrodes, noticing the difference between their readings when the current was allowed to pass in different directions. He graduated them in terms of heat units by sending a current through a spiral coil of fine wire enclosing one of the bulbs. The values of H which he so obtained compare fairly well with those of $t(dE/dt)$ measured directly. This method seems to depend rather too much on the steadiness of convection currents in a liquid to be quite reliable, and I have tried several arrangements to avoid this difficulty with, I think, satisfactory results.

Some very good observations were obtained with an apparatus on the ordinary calorimeter principle. It was made up of the following parts, fig. 6:—

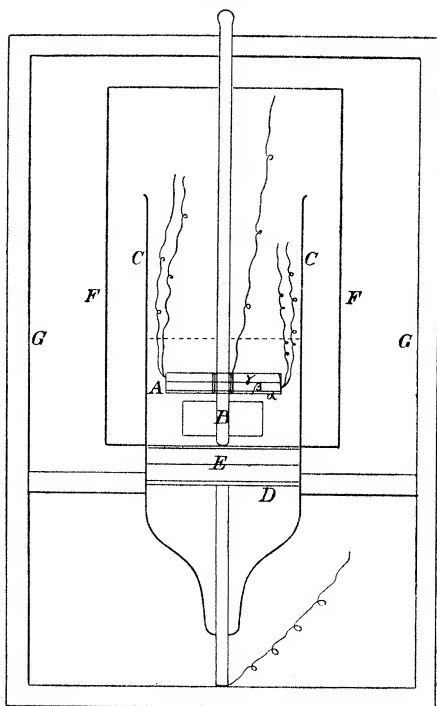
A. *The Measuring Apparatus.*—This consists of a double bobbin of thin sheet copper on a hollow core, on the lower end of which is screwed a metal plate (α), which forms the electrode, and is in close proximity all over its inner surface with the lower side of the bobbin. The lower half of the bobbin (β) is wound with very fine copper wire, the resistance of which forms the thermometer. The upper half of the bobbin (γ) is wound with platinoid wire, having a resistance of 9.58 ohms. This platinoid coil formed the heater, by means of which a known quantity of heat could be put into the calorimeter, and in this way its heat capacity could be measured.

B is a revolving stirrer which passes through the core of A, and rests on a thin metal plate.

The calorimeter vessel, C, is a thin glass tube, drawn out at its lower extremity, through which passes the stem of the lower electrode, D, which is a circular plate of metal; over D are porous plates, E, protected from the stirrer by a thin sheet of metal.

All the vessel above this sheet of metal is enclosed in a metal box F, and all above D is in a wooden box, G, which is surrounded on all sides by fossil meal.

FIG. 6.



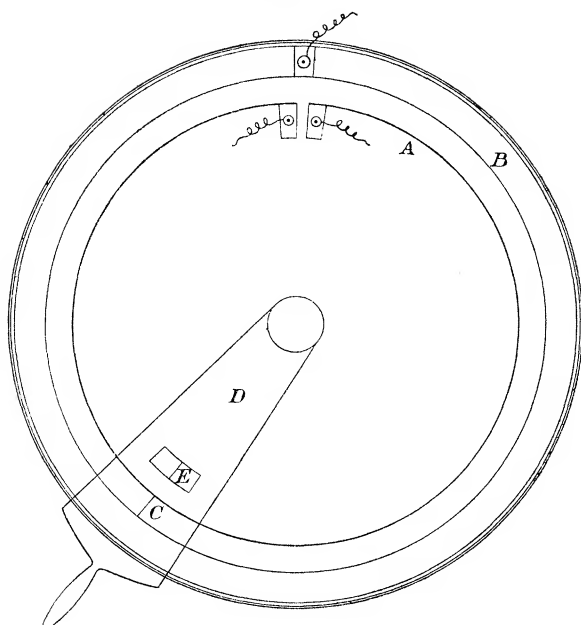
The solution under examination is put in C, so as to cover A to a depth of half an inch, or thereabouts.

For measuring the current, the potential between the ends of a known resistance in its circuit was compared with a Clarke cell. Thus, if on the potentiometer the latter = S, the former = RC being T, we have

$$RC = (T/S) 1.434 \text{ volt.}$$

For measuring the resistance, or rather the change in the resistance, of the coil B, a circular wire bridge, of what is believed to be a new form (fig. 7), which entirely avoids all thermoelectric disturbance, was used. The bridge wire, A, is on the inside wall of a circular channel, cut in a thick piece of wood. A second wire, B, made of the same material as A, is sprung into a groove on the outside wall of the channel. The ends of A are on two copper plates close together, and the ends of B are on a copper plate just opposite them, on the other side of the channel, so that all the junctions of dissimilar metals are within an area of about 1 sq. in. Contact is made between

FIG. 7.



A and B by a wire, C, of the same material, fixed on a handle, D, the position of which is read on a scale by a pointer, E. -

A switchboard was used which allowed a current to be sent in either direction through the liquid in the calorimeter, or through the coil, γ , or through both at once.

Two methods were employed with this apparatus for measuring the Peltier effect at α . The first is as follows.

After all has attained a uniform temperature, the resistance of β is measured. A current was then passed through γ for three minutes, the liquid being well stirred, and the current being measured. The resistance of β is again measured.

The whole is allowed to stand for a few minutes till the temperature is steady, and then a current is passed through the liquid by the plate α for three minutes, and the resistance of β is again measured. After a rest the current is reversed, and allowed to pass again through the liquid, and the resistance is again measured.

When the current is passing through the liquid the heating effect is due to two causes; one of these is unknown, and is independent of the direction of the current. Let C be the current, and let Ac^2 be this unknown heat. The rest is due to the Peltier effect, and we may put it equal to Hc .

Let d_1, d_2, d_3 be the changes in the resistance of β in the three observations, R the resistance of the platinoid coil γ , C_1 the current in the first, C that in the latter two observations. Then we have the following equations, since we may take d_1, d_2, d_3 proportional to the changes in the temperature :—

$$\begin{aligned} RC_1^2 &= d_1 K \\ AC^2 + HC &= d^2 K \\ AC^2 - HC &= d_3 K \\ 2HC &= (d_2 - d_3) K \\ H &= \frac{d_2 - d_3}{2d_1} \cdot \frac{C_1^2}{C} \cdot R \end{aligned}$$

This is open to the objection that the heating not being the same in each case, the loss of heat will not be the same in each.

An improvement on this method which was afterwards adopted ensures the loss of heat being steady, and the same for all the observations. This was to so adjust the current that the change in the resistance of β should be the same, whether the current passed through the liquid, so as to heat the electrode α , or whether it passed so as to cool α , and at the same time passed through the coil γ .

If C is the current which gives these equal differences, we have

$$AC^2 + HC = dK = AC^2 - HC + RC^2,$$

or

$$H = \frac{1}{2} RC.$$

The following observations were obtained with these methods, or combination of them, using a 15 per cent. solution of copper sulphate, for which the value of $\mathcal{J}$ was equal to 6.8. The current is given in terms of potentiometer readings and the change of resistance in bridge divisions.

Current 311 through γ gives $d = 49.6$.

Current +315 through liquid gave $d = +11$.

„ -315 „ „ „ $d = -39, -39.5, -40, -43,$
and -46 .

Mean, -41.5 .

Mean of first three, -39.5 .

+11 and -41.5 give $H = 0.1992$. $H/t = 6.94 \times 10^{-4}$.

+11 and -39.5 „ $H = 0.1927$. $H/t = 6.72 \times 10^{-4}$.

Current -311 gave the same change of resistance as current $+306$ through liquid α coil γ ,

whence

$$H = 0.1956,$$

$$H/t = 6.815 \times 10^{-4}.$$

Current 335 by the second method gave perfectly constant change 34 of resistance for both directions of current,

whence

$$H = 0.2078,$$

$$H/t = 7.24 \times 10^{-4}.$$

Finally, the measurement was reduced to a null method by using two pieces of apparatus like A, of the same size, and as nearly alike as possible. These were used side by side in a wooden bowl of liquid of an oblong shape, with a copper bottom, and divided by an ebonite plate, so that the current from the electrodes should go vertically through the liquid. Each platinoid coil had a resistance = 12.35 ohms., and the thermometer coils were 32 and 36 ohms. respectively. The total thickness of each bobbin with its electrode plate was not much above $\frac{1}{4}$ in., the diameter a little over 1 in.

The current passes through one of the γ coils, and from one electrode plate to the other through the bottom of the liquid. It is adjusted so that the ratio of the resistances of the thermometer coils should remain constant for both directions of current.

We now have, using the same letters as before, the single equation

$$AC^2 + HC = AC^2 - HC + RC^2,$$

assuming everything symmetrical,

or

$$H = \frac{1}{2}RC.$$

If there is any want of symmetry, we shall get two values for C, one for each direction of the current, and if these are nearly equal, we are safe in taking their mean.

With this apparatus for the same solution a perfect balance was got in each direction for the same value of $C = 0.0339$ amp.

$$\therefore H = 6.165. \quad C = 0.2091 \text{ volt amp.}$$

$$H/t = 7.26 \times 10^{-4}.$$

As this seemed rather high, the contact of the electrodes with the bobbins was made better by amalgamating their surfaces.

A current 280 potentiometer gave a bridge change -10 in 5'.

„ 260 „ „ „ „ +17

Mean 272.6 should give balance.

Current 272 gave perfect balance in each direction for different lengths of time.

This gives $H = 0.1952. \quad t = 286.$

$$H/t = 6.83 \times 10^{-4}.$$

This the last, and, I believe, the best, result, is almost exactly equal to $\mathcal{P}$ for the solution.

With the last apparatus and a solution of nitrate of copper, for which $\mathcal{P}$ was measured and found = 6.14, a perfect balance in both directions was obtained

with $C = 245$ potentiometer

$$R = 1.05 \quad ,,$$

$$S = 11.695 \quad ,,$$

$$H = 0.1764. \quad t = 288.$$

$$H/t = 6.1 \times 10^{-4}.$$

I should have liked to do a few more solutions, but something went wrong with the insulation of the bobbins, and I had no time to repair them. However, these two results appear to be enough to enable us to say that the equation

$$dE/dt = H/t$$

is true for the junctions of the kind under examination, and that these thermo-electric phenomena are reversible.

VII. "Experimental Determination of Poisson's Ratio." By
C. E. STROMEYER. Communicated by LORD KELVIN, P.R.S.
Received April 12, 1894.

The experiments with which this paper deals were carried out between the years 1883 and 1886 by Professor Kennedy and the author, with an instrument which the latter had originally designed for measuring local strains in metal structures, but which proved itself to be so exceedingly sensitive that it seemed capable of being applied to the measuring of the cross contraction of test pieces while these were subjected to a longitudinal pull, thus providing the means for measuring Poisson's ratio direct. In its original form the instrument consisted of two small frames, which were secured to each other by means of two flat springs, in such a manner, that any relative motion was a perfectly parallel one. One of these frames carried a small piece of dark glass, and close to it, but on the other frame, a right-angled reflecting glass prism was secured. The two glass surfaces, which faced each other, were then carefully adjusted, so as to

FIG. 1.

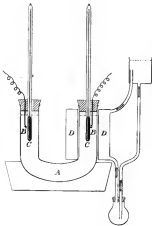
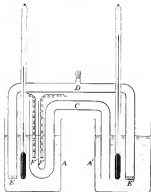


FIG. 5.



AA' are two beakers containing one of the liquids under examination, which we will call No. 1.

BB' are two thermometers for telling the temperature of the liquid in the beakers.

C is a bent tube full of No. 1 liquid, which is continuous between the end of *C*, which is under the liquid in *A'*, and in which the electrode *F'* dips.

D is a siphon tube connecting the liquids in *AA'*; it is full of liquid No. 2, and is closed at its ends by porous plugs, *EE'*, made of porous earthenware and fixed with shells.

FF' are the electrodes, *F* being in beaker *A*, and *F'* in tube *C*, close to *F*, the bent part of *C* being in the beaker *A*.